

HYDROGEN PLASMA PHOTORESIST STRIP AND POLYMERIC  
RESIDUE CLEANUP PROCESS FOR OXYGEN-SENSITIVE  
MATERIALS

CROSS-REFERENCE TO RELATED PATENT/PATENT APPLICATIONS

The following commonly assigned patent/patent applications are hereby incorporated herein by reference:

<u>Patent No./Serial No.</u>	<u>Filing Date</u>	<u>TI Case No.</u>
		TI-26189

FIELD OF THE INVENTION

The instant invention pertains to semiconductor device fabrication and processing and more specifically to post metal pattern and etch clean-up processing.

BACKGROUND OF THE INVENTION

Most semiconductor devices utilize several different levels of metallization. With the increasing complexity of devices and the need to reduce the physical size of devices, the number of levels which incorporate metal connections is increasing. In addition, with the desire to increase the speed of the devices while reducing the power consumed by the devices, advanced metallization schemes are being developed. One such scheme involves the use of copper-doped aluminum or copper structures for the bus lines and interconnects. Additionally, interlevel dielectrics with lower dielectric constants than standard silicon dioxide films may be used as the dielectric material situated between metallic structures.



For a typical Cu metallization scheme, a standard O<sub>2</sub> plasma ash is performed to remove photoresist after a via etch process. Since ashing with O<sub>2</sub> causes substantial oxidation to any exposed Cu at the bottom of the via, the via etch process generally completes to the Si<sub>3</sub>N<sub>4</sub> barrier layer typically deposited to prevent Cu oxidation. The nitride layer must then be removed in a separate wet or dry etch process. Thus, a dry plasma etch process which could be used to remove photoresist without oxidation of Cu would simplify the process flow by either eliminating the need for the Si<sub>3</sub>N<sub>4</sub> barrier layer, or substantially thinning it (it might still be useful as an etch stop layer for via formation). Removal or thinning of the Si<sub>3</sub>N<sub>4</sub> barrier layer would ease the oxide etch selectivity requirements since stopping the etch on the Si<sub>3</sub>N<sub>4</sub> layer would not be necessary.

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## SUMMARY OF THE INVENTION

An embodiment of the instant invention is a hydrogen-containing plasma processing step to be used after the metal structure is etched. This novel step will passivate most metal structures, remove the polymeric residue from the sidewalls of the metal structures, and will remove the photoresist. In addition, this novel step has the following advantages over the prior art methods: it is a higher throughput process, it can be done in situ in any resist strip equipment regardless of the plasma energy source (e.g. a downstream microwave plasma source or a conventional RF plasma source), it provides better passivation of the exposed metal pattern by converting the metal halide residues into volatile hydrogen halides, it does not substantially oxidize the exposed Cu and therefore may be used in structures without Cu-barrier layers present, it does not produce hazardous waste, and it does not corrode the processing equipment.

An embodiment of the instant invention is a method of fabricating an electronic device formed on a semiconductor wafer, the method comprising the steps of: forming a layer of a first material over the substrate, the first material is oxygen-sensitive; forming a photoresist layer over the layer of the first material; patterning the layer of the first material; removing the photoresist layer after patterning the layer of the first material; and subjecting the semiconductor wafer to a plasma which incorporates a gas which includes hydrogen or deuterium so as to remove residue from the first material. Preferably, the step of removing the photoresist layer is performed by subjecting the semiconductor wafer to the plasma which incorporates a gas which includes hydrogen or deuterium; or it is performed by subjecting the semiconductor wafer to a higher temperature step which is conducted in a hydrogen ambient with a plasma impinging upon the semiconductor wafer. The higher temperature is, preferably, around 245 °C.

In an alternative embodiment, the gas additionally includes a forming gas. Preferably, the forming gas is comprised of a gas consisting of: argon, nitrogen, and any other inert gas.

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Preferably, the first material is comprised of a conductive material. More specifically, the first material is, preferably, comprised of: copper, tantalum, titanium, titanium nitride, tungsten, tungsten nitride, aluminum, copper-doped aluminum, silver, gold, and any combination thereof.

Another embodiment of the instant invention is a method of forming a conductive feature comprised of an oxygen-sensitive material over a semiconductor substrate for an electronic device, the method comprising the steps of: forming a conductive layer over the semiconductor substrate, the conductive layer comprised of the oxygen-sensitive material; forming a photoresist layer over the conductive layer, the photoresist having a pattern so as to expose portions of the conductive layer; removing the exposed portions of the conductive layer so as to form the conductive structure; and subjecting the semiconductor wafer to a plasma which incorporates a gas which includes hydrogen or deuterium. Preferably, the oxygen-sensitive material is comprised of copper, tungsten, tungsten nitride, tantalum, titanium, TiN, aluminum, copper-doped aluminum, silver, or gold.

Another embodiment of the instant invention is a method of fabricating a conductive interconnect for providing an electrical connection between a first conductor and a second conductor for an electrical device formed in a semiconductor substrate, the method comprising the steps of: forming a dielectric layer on the first conductor, the dielectric layer having at least one opening which exposes the first conductor; forming a layer of an oxygen-sensitive material on the dielectric layer, the oxygen-sensitive material substantially filling the opening in the dielectric layer and for providing an electrical contact to the first conductor; forming a photoresist layer on the oxygen-sensitive material, the photoresist layer having a pattern so as to expose portions of the oxygen-sensitive material; removing the exposed portions of the oxygen-sensitive material on the dielectric material, the removal step causing a residue to be formed on exposed surfaces of the remaining portions of the oxygen-sensitive

material; and removing the photoresist layer by subjecting the photoresist layer with a hydrogen-containing gas incorporated into a plasma. Preferably, the oxygen-sensitive material is comprised of a material selected from the group consisting of: copper, tungsten, tungsten nitride, tantalum, titanium, titanium nitride, aluminum, copper-doped aluminum, silver, gold, and any combination thereof. This embodiment of the instant invention may further comprising the step of: removing the residue by subjecting the residue to a fluorinated etchant, where the fluorinated etchant is, preferably comprised of  $\text{CF}_4$  or  $\text{CHF}_3$ .

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### BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a flow diagram illustrating the method of one embodiment of the instant invention. This method is preferably utilized in a damascene process flow where oxygen-sensitive (metal) structures are exposed (during the via etch process, preferably).

FIGURES 2a-2e are cross-sectional views of a semiconductor device which is fabricated using the method of the instant invention (which is illustrated in FIGURE 1). This damascene flow is preferably utilized when oxygen sensitive metal will be exposed (during the via etch process, preferably).

FIGURE 3 is a flow diagram illustrating the method of another embodiment of the instant invention. This method is preferably utilized in a dual damascene process flow where oxygen-sensitive (metal) structures are exposed (during the via etch process, preferably).

FIGURES 4a-4h are cross-sectional views of a semiconductor device which is fabricated using the method of the instant invention (which is illustrated in FIGURE 3), incorporated into a dual damascene process flow where oxygen sensitive metal is exposed (during the via etch process, preferably).

FIGURE 5 is a flow diagram illustrating the method of another embodiment of the instant invention. This method of the instant invention is preferably utilized in a process flow where any exposed structures may or may not be oxygen-sensitive.

FIGURES 6a-6d are cross-sectional views of a semiconductor device which is fabricated using the method of the instant invention (which is illustrated in FIGURE 5) incorporated into a non-damascene process, such as that used for Al metallization, for example.

### DETAILED DESCRIPTION OF THE DRAWINGS

While the methods of the instant invention are described with reference to FIGURES 1-6, the methods of the instant invention can be applied to any type of device

structure (*e.g.* metal interconnects, metal lines, metal gates, or other conductive structures) and to any type of device (*e.g.* memory devices, logic devices, power devices, DSPs, or microprocessors). In addition, the method of the instant invention can be used to remove residue and/or photoresist from other device structures. Furthermore, while the methods of the instant invention, as described below, revolve around the use of hydrogen plasma, other plasmas may be used (such as a deuterium plasma, or other hydrogen- containing plasmas, such as  $\text{NH}_3$ ,  $\text{N}_2\text{H}_2$ ,  $\text{H}_2\text{S}$  and  $\text{CH}_4$ , and deuterated forms of these gases, for example).

The following method of one embodiment of the instant invention should preferably be used in a process flow where there are exposed portions of oxygen-sensitive conductive structures.

Referring to FIGURE 1 and FIGURE 2a, after providing substrate 202, isolation region 204 (which could be formed using LOCOS, field oxidation, or shallow trench isolation techniques), source/drain regions 208, gate dielectric 212, conductive gate structure 210, sidewall insulators 214, dielectric layer 216 (preferably comprised of BPSG, PSG, silicon oxide, oxide/nitride stack, TEOS, a low dielectric constant material, or any other interlevel dielectric material – in fact, regions 216 and 218 can be one layer), liner/barrier layer 220 (preferably comprised of Ti, TiN, or a Ti/TiN stack), conductor 222 (preferably comprised of aluminum, copper, copper-doped aluminum, or any other refractory metal), barrier layer 224 (preferably comprised of silicon nitride), dielectric layer 226 (preferably comprised of BPSG, PSG, TEOS, aerogel, xerogel, HSQ or any other low dielectric constant material), photoresist layer 230 is formed and patterned (step 102) over dielectric layer 226. Preferably, dielectric layer 226 is comprised of an oxide, an oxide/nitride stack, BPSG, PSG, TEOS, or a low dielectric constant material, such as aerogel, xerogel, HSQ, or a polymer. Opening 227 in photoresist 230 is preferably aligned with underlying metal structure 222, which may be surrounded by liner/barriers 220 and 224, as in the case of Cu metallization, for example, when the metal is oxygen sensitive. Preferably, conductive structure 222 is a



conductive line which is connected to other lines by interconnects and/or vias. Conductive structure 222 (for the damascene structure) is preferably comprised of copper or copper-doped aluminum (preferably on the order of 0.5 to 2.5 wt% of copper in aluminum). Liner/barriers 220 and 224 are comprised of titanium, titanium nitride, a Ti/TiN stack or other barrier-like material which adheres well to copper, aluminum and the interlevel dielectric material 218. Liner/barriers 220 and 224 may be comprised of the same material(s), but they do not have to be.

Referring to step 104 of FIGURE 1 and FIGURE 2b, an opening 228 is formed in dielectric 226 and liner/barrier layer 224 so as to expose at least a portion of conductor 222. Preferably, this is accomplished by subjecting the semiconductor wafer to  $CF_4$ ,  $CHF_3$ , or other fluorinated compound plasma environment.

Referring to steps 106 and 108 of FIGURE 1 and FIGURE 2c, in order to remove photoresist layer 230, passivate the exposed portion of conductor 222, and clean any polymer layers off of the exposed portions of conductor 222, the method of the instant invention is utilized. Using the method of the instant invention, photoresist 230 can be removed at the same time that the clean and passivation steps are performed. Preferably, in step 106 the photoresist is removed by subjecting the wafer to a photoresist removal step which uses a remote (or downstream) plasma and substantially no oxidizing chemical component. Hence, using the instant invention, the photoresist can be removed by subjecting it to a hydrogen-containing (with or without the addition of argon or nitrogen) or deuterium-containing photoresist removal process which uses a remote or downstream plasma. This may be followed by additional processing which includes subjecting the wafer to another hydrogen-containing etch process which preferably uses a remote or downstream plasma so as to remove any residue. Both of these process steps can be accomplished in Mattson, Applied Materials ASP, GaSonics International, or Fusion ashers or other similar processing tools. The hydrogen could be introduced with a forming gas such as  $N_2$  or Ar (where the hydrogen is 60 to 100% of the mixture) and/or deuterium may be used instead of hydrogen. If conductor 222 contains copper or other oxygen-sensitive material, and the



and residue due to step 108). Preferably, liner/barrier 232 is comprised of a material which will act as a barrier, will adhere to dielectric layer 226, will act as an adhesion layer for conductor 234, and which is electrically conductive (more preferably liner/barrier 232 is comprised of Ti, TiN, or a Ti/TiN stack). Next, conductor 234 is formed, preferably by electroplating or PVD. Conductor 234 is preferably comprised of aluminum, copper doped aluminum, copper, or other conductor or refractory metal.

Referring to step 112 of FIGURE 1 and FIGURE 2e, conductor 234 is planarized so as to form interconnect 234. Preferably, the planarization is accomplished by chemical-mechanical polishing (CMP) or a blanket etch-back process. Liner/barrier 232 may remain intact (as is shown in FIGURE 2e), or the portions of liner/barrier 232 above dielectric 226 may be removed. This may be done during the planarization step or it may be done separately. Further processing can be performed using standard device processing techniques which would be obvious to one of ordinary skill in the art.

Referring to step 302 of FIGURE 3 and FIGURE 4a, after providing substrate 402, isolation region 404 (which could be formed using LOCOS, field oxidation, or shallow trench isolation techniques), source/drain regions 406, gate dielectric 408, conductive gate structure 412, sidewall insulators 410, dielectric layer 414 (preferably comprised of BPSG, PSG, silicon oxide, oxide/nitride stack, TEOS, a low dielectric constant material, or any other interlevel dielectric material – in fact, regions 414 and 416 can be one layer) liner/barrier layer 418 (preferably comprised of Ti, TiN, or a Ti/TiN stack), conductor 420 (preferably comprised of aluminum, copper, copper-doped aluminum, or any other refractory metal), barrier layer 422 (preferably comprised of silicon nitride), dielectric layer 424 (preferably comprised of BPSG, PSG, TEOS, aerogel, xerogel, HSQ or any other low dielectric constant material), photoresist layer 428 is formed and patterned over hardmask layer 426. Preferably, hardmask layer 426 is comprised of an oxide, an oxide/nitride stack, or silicon nitride (most preferably, it is comprised of a nitride).

Using the photoresist as a mask, hardmask 426 is etched so as to create opening 427 in the hardmask. Opening 427 is preferably aligned with underlying metal structure 420.

Referring to step 304 of FIGURE 3 and FIGURE 4b, photoresist 428 is removed. This may be accomplished by using a traditional oxygen ash step followed by a clean-up step, or the method of one embodiment of the instant invention can be used. Using the method of the instant invention, the wafer is subjected to a hydrogen-containing plasma so as to remove the photoresist and any residue. Preferably, the wafer temperature during this step is on the order of 150 to 350 °C (more preferably around 240 to 250 °C). While a hydrogen plasma is preferable, one or more forming gases (such as N<sub>2</sub> or Ar) can be added and/or deuterium or other hydrogen-containing gases such as NH<sub>3</sub>, N<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>S, or CH<sub>4</sub>, or deuterated forms of these gases, for example, may be used instead of hydrogen. A subsequent clean-up step can be performed but it is not necessary.

Referring to step 306 of FIGURE 3 and FIGURE 4c, a dielectric material is formed on hardmask 426. Preferably, dielectric layer 430 is comprised of TEOS, BPSG, PSG, HSQ, or a low dielectric constant material, such as aerogel, xerogel, or a polymer (such as fluorinated parylene). Dielectric layer 430 is preferably either spun on or deposited using chemical vapor deposition (CVD).

Referring to step 308 of FIGURE 3 and FIGURE 4d, photoresist layer 432 is formed with a pattern. This is followed by an etch process to remove the exposed portions of dielectric layers 430 and 424, and create via opening 429. Preferably, this etch process is an anisotropic process, and, more preferably, it is performed using CHF<sub>3</sub>, CF<sub>4</sub>, or other fluorinated hydrocarbon plasma chemistry. Referring to step 310 of FIGURE 3 and FIGURE 4e, an overetch process is performed to ensure completion of the dielectric etch. The barrier layer 422 is then removed (preferably using a fluorine-based plasma chemistry to remove Si<sub>3</sub>N<sub>4</sub>, for example) to expose the metal (Cu) layer 420.

Referring to step 312 of FIGURE 1 and FIGURE 4f, photoresist 432 is removed. This may be accomplished by using a traditional oxygen ash step followed by a clean-

up step, or the method of one embodiment of the instant invention can be used. The traditional oxygen ash step should not be performed if the exposed metal structure is comprised of a material that is oxygen sensitive (such as copper or copper doped aluminum). If a traditional photoresist removal step is performed, a subsequent clean-up step must be performed. The preferable clean-up step would include the method of the instant invention. More specifically, the wafer would be subjected to a hydrogen or deuterium containing plasma (which may also contain a forming gas such as N<sub>2</sub> or Ar) at a wafer temperature around 150 to 350 °C. This clean-up step of the instant invention will remove any hydrocarbon residue left on metal structure 420 and will passivate metal structure 420.

Using the method of the instant invention to remove the photoresist, the wafer is subjected to a hydrogen-containing plasma so as to remove the photoresist and any residue resulting from the reaction of the anisotropic oxide etch chemistry with the photoresist layer. Preferably, the wafer temperature during this step is on the order of 150 to 350 °C (more preferably around 240 to 250 °C). While a hydrogen plasma is preferable, one or more forming gases (such as N<sub>2</sub> or Ar) can be added and/or deuterium or other hydrogen-containing plasmas, such as NH<sub>3</sub>, N<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>S, or CH<sub>4</sub>, or deuterated forms of these gases, for example, may be used instead of hydrogen. A subsequent clean-up step can be performed but it is not necessary. The photoresist removal step may be followed by another hydrogen or deuterium step to further clean any residue left on exposed metal structure 420 and to passivate metal structure 420. This step is optional, since both of these advantages will be accomplished, to some extent, during the photoresist strip step of the aforementioned embodiment of the instant invention.

Referring to step 314 of FIGURE 3 and FIGURE 4g, a metal or other conductive material is formed over the liner 434. Liner layer 434 is preferably comprised of Ti, TiN, or a Ti/TiN stack. Preferably, metal layer 436 is comprised of aluminum, copper, copper-doped aluminum (preferably on the order of 0.5 to 5%; more preferably on the

order of 1 to 2%), or any other refractory metal. Metal layer 436 is preferably formed by electroplating, PVD or CVD or a combination thereof.

Referring to step 316 of FIGURE 3 and FIGURE 4h, metal structure 436 is planarized so as to form via and conductive line 438. Preferably, this planarization step is accomplished by CMP or a blanket etch-back step. The portion of liner/barrier 434 which is situated above dielectric 430 may be removed during this step, or it can be removed in a subsequent step.

While FIGURES 1-4h illustrate two different types of damascene process, the instant invention can be used on any type of damascene process or any other type of metallization process. One of ordinary skill in the art should be able to extrapolate the use of the instant invention in many different types of structure formation schemes based on his or her knowledge and the teachings in the instant specification.

The embodiment of the instant invention illustrated in FIGURES 5 and 6a-6d preferably utilizes a metal structure which is comprised of aluminum or aluminum doped with a smaller amount of copper (preferably on the order of 0.5 to 2 wt%; hence, a conductive structure which is not substantially sensitive to an oxygen ambient. While Cu doping of Al improves the electromigration resistance of the interconnect, pure copper structures and aluminum structures with greater than 5% copper doping are difficult to etch. The instant invention would work for such structures, in addition to pure Cu structures, if they could be etched.

Referring to step 502 of FIGURE 5 and FIGURE 6a, conductive stack 619 is formed above dielectric layers 616 and 614 (which may be formed in a single layer). Preferably, dielectric layers 614 and 616 are comprised of the same material which may include: BPSG, PSG, HSQ, silicon oxide, TEOS, or a low dielectric constant material (such as aerogel, xerogel, or a low-k polymer such as fluorinated parylene). An underlying structure may include: isolation region 604 (which may be comprised of a shallow trench isolation structure, a field oxide region, or a LOCOS region);

Preferably, conductive stack 619 is comprised of titanium containing layer 618, titanium nitride containing layer 620, conductor 622, and an antireflective coating (ARC) 624. Preferably, conductor 622 is comprised of aluminum or copper-doped aluminum (where there is 0.5 to 2.5 wt% of copper), and ARC layer 624 is comprised of TiN, and optionally, an inorganic layer (such as  $\text{SiO}_x\text{N}_y$ ) or organic layer on top of the TiN layer. While layers 618, 620, and 624 are described herein to contain titanium or titanium nitride, these exact compositions are not necessary, they are merely the best choices for adhesion and barrier properties using present processing technologies. It should be obvious to one of ordinary skill in the art to use other combinations of materials.

Referring to step 504 of FIGURE 5 and FIGURE 6b, a patterned photoresist layer 626 is formed on ARC layer 624 by a sequence typically consisting of photoresist coating, lithographic patterning and developing, so as to provide a pattern for a subsequent conductor patterning step. Referring to step 506 of FIGURE 5 and FIGURE 6c, conductive stack 619 is patterned using photoresist layer 626 as a pattern mask. Preferably, step 506 is accomplished by a commercial metal etch reactor, such as an Applied Materials DPS reactor or a Lam Research Corporation TCP 9600 plasma reactor. In the case that an additional inorganic (such as  $\text{SiO}_x\text{N}_y$ ) or organic layer is used on top of the TiN ARC layer, this layer has to be opened prior to etching the conductive stack. Other than patterning conductive stack 619, the result of this step is to erode portions of photoresist layer 626 which forms a polymeric residue on conductors 625 and on the exposed portions of dielectric layer 616. The remaining photoresist and the residue must be removed.

Referring to steps 508 and 510 of FIGURE 5 and FIGURE 6d, photoresist 626 is removed next. Traditionally, photoresist 626 was removed by subjecting the wafer to an oxygen-containing ambient at an elevated temperature. In addition, an H<sub>2</sub>O-containing plasma has to be used to convert aluminum halide, which is the main etch byproduct and is the cause of aluminum corrosion if left on the etched surface, into volatile hydrogen halide. This may not be applicable in some processing chambers and it may cause problems if conductor 622 is comprised of an oxygen-sensitive material. In addition, if the traditional method is utilized, a subsequent clean-up step must be performed so as to remove any residue formed on the conductive structure. This clean-up step may utilize a solvent (wet) clean or it may utilize the (dry) clean-up step of the instant invention.

The method of the instant invention can be used to remove the photoresist, clean any residue, including aluminum halide, formed on the conductive structures and on the dielectric, and to passivate the conductive structure. Preferably, the method of the instant invention is comprised of subjecting the wafer to a hydrogen-containing or deuterium-containing plasma (preferably a remotely generated plasma) at an ambient temperature around 150 to 350 °C (more preferably around 200 to 260 °C – even more preferably around 240 to 250 °C). Alternatively, a multiple step ash and clean process may be used which includes both the H<sub>2</sub> or hydrogen- containing plasma and the conventional H<sub>2</sub>O/ O<sub>2</sub> plasma processes. In an alternative embodiment, the residue removal step of the instant invention is performed prior to the removal of the photoresist (where accomplished using the method of the instant invention or not).

While the embodiments of the instant invention are described above with regards to removing residue from metallic structures, the instant invention is equally applicable to removing residue from the sidewalls and other exposed portions of the dielectric layer. More specifically, residue, which is produced by the reaction of the photoresist with the fluorine-containing chemistry (used to etch the openings in the dielectric layers – preferably comprising an oxide) forms both on the underlying



metallic structure and on the exposed portions of the dielectric layer and is readily removed using any of the embodiments of the instant invention. Hence, when vias or openings are formed in the dielectric layers (which are covered with pattern photoresist), residues form on the sidewalls of the vias/openings in the dielectric layer and on the portion of the underlying conductor which is exposed by this newly formed via/opening in the dielectric layer. This residue can be removed by the methods of the instant invention.

Although specific embodiments of the present invention are herein described, they are not to be construed as limiting the scope of the invention. Many embodiments of the present invention will become apparent to those skilled in the art in light of the methodology of the specification. The scope of the invention is limited only by the claims appended.

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